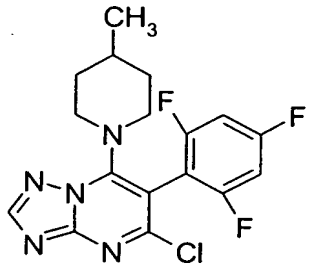
10/591290
IAP12 Rec'd PCT/PTO 31 AUG 2006

Ternary fungicidal mixtures

Description

The present invention relates to ternary fungicidal mixtures comprising, as active components,

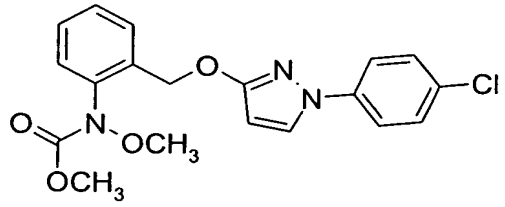
1) the triazolopyrimidine derivative of the formula I



I

and

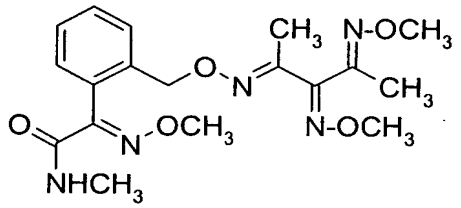
2) a strobilurin derivative II, selected from among the compounds pyraclostrobin II-1



II-1

and

orysastrobin II-2



II-2

and

3) a fungicidally active compound III selected from the group consisting of

acylalanines, amine derivatives, anilinopyrimidines, antibiotics, azoles, dicarboximides, dithiocarbamates, copper fungicides, nitrophenyl derivatives, phenylpyrroles, sulfenic acid derivatives, cinnamides and analogs and anilazine, benomyl, boscalid, carbendazim, carboxin, oxycarboxin, cyazofamid, dazomet, dithianon, famoxadone, fenamidone, fenarimol, fuberidazole, flutolanil, furametpyr, iso-

prothiolane, mepronil, nuarimol, picobenzamid, probenazole, proquinazid, pyrifenox, pyroquilon, quinoxyfen, silthiofam, thiabendazole, thifluzamide, thiophanate-methyl, tiadinil, tricyclazole, triforine, sulfur, acibenzolar-S-methyl, benthiavalicarb, carpropamid, chlorothalonil, cyflufenamid, cymoxanil, dazomet, diclomezin, diclocymet, diethofencarb, edifenphos, ethaboxam, fenhexamid, fentin acetate, fenoxanil, ferimzone, fluazinam, phosphorous acid, fosetyl, fosetyl-aluminum, iprovalicarb, hexachlorobenzene, metrafenon, pencycuron, propamocarb, phthalide, toloclofos-methyl, quintozene and zoxamide

in a synergistically effective amount.

Moreover, the invention relates to a method for controlling phytopathogenic harmful fungi using mixtures of the compounds I and II and III with a fungicidally active compound III and to the use of the compounds I and II with III for preparing such mixtures, and to compositions comprising these mixtures.

The compound I, 5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, its preparation and its action against harmful fungi are known from the literature (WO 98/46607).

The strobilurin derivatives II are also known in the literature (WO 96/01256; WO 97/15552). Mixtures of the strobilurin derivatives II with various other fungicidally active compounds have also been described in the literature.

Mixtures of the compound I with the strobilurin derivatives II-1 and II-2 are described in WO 04/045289 and WO 04/045283, respectively.

Mixtures of triazolopyrimidine derivatives with various fungicidally active compounds are proposed in a general manner in EP-A 988 790. The compound I is embraced by the general disclosure of this publication, but not explicitly mentioned. Mixtures of triazolopyrimidines with two further fungicidally active compounds are not proposed. Accordingly, the ternary mixtures are novel.

The synergistic mixtures, disclosed in EP-A 988 790, of triazolopyrimidines are described as being fungicidally active against various diseases of cereals, fruit and vegetables, in particular mildew on wheat and barley or gray mold on apples.

Practical agricultural experience has shown that the repeated and exclusive application of an individual active compound in the control of harmful fungi leads in many cases to a rapid selection of those fungus strains which have developed natural or adapted

resistance against the active compound in question. Effective control of these fungi with the active compound in question is then no longer possible.

To reduce the risk of the selection of resistant fungus strains, mixtures of different active compounds are nowadays conventionally employed for controlling harmful fungi. By combining active compounds having different mechanisms of action, it is possible to ensure successful control over a relatively long period of time.

It is an object of the present invention to provide, with a view to effective resistance management and effective control of phytopathogenic harmful fungi, at application rates which are as low as possible, mixtures which, at a reduced total amount of active compounds applied, have improved activity against the harmful fungi (synergistic mixtures).

The mixtures defined at the outset have accordingly been found. Moreover, we have found that with simultaneous, that is joint or separate, application of the compounds I and II and one of the compounds III or successive application of the compound I and II and one of the compounds III, better control of harmful fungi can be achieved than is possible with the individual compounds.

The invention preferably provides mixtures of the compound I with pyraclostrobin II-1 and a compound III. They are particularly advantageous for controlling harmful fungi from the class of the *Oomycetes*.

The invention furthermore preferably provides mixtures of the compound I with orysastrobin II-2 and a compound III. They are particularly advantageous for controlling rice-pathogenic harmful fungi from the classes of the *Ascomycetes*, *Deuteromycetes* and *Basidiomycetes*.

In addition, the above-mentioned mixtures of the compounds I and II and the compounds III or the simultaneous, that is joint or separate, use of the compounds I, II and a compound III are/is highly effective against a wide range of phytopathogenic fungi, in particular from the classes of the *Ascomycetes*, *Deuteromycetes*, *Oomycetes* and *Basidiomycetes*. Some of them act systemically and can be used in crop protection as foliar fungicides, as fungicides for seed dressing and as soil-acting fungicides.

They are particularly important for controlling a multitude of fungi on various cultivated plants, such as bananas, cotton, vegetable species (for example cucumbers, beans and cucurbits), barley, grass, oats, coffee, potatoes, corn, fruit species, rice, rye, soya,

tomatoes, grapevines, wheat, ornamental plants, sugar cane and also on a large number of seeds.

They are particularly suitable for the control of the following phytopathogenic fungi: *Blumeria graminis* (powdery mildew) on cereals, *Erysiphe cichoracearum* and *Sphaerotheca fuliginea* on cucurbits, *Podosphaera leucotricha* on apples, *Uncinula necator* on grapevines, *Puccinia* species on cereals, *Rhizoctonia* species on cotton, rice and lawns, *Ustilago* species on cereals and sugar cane, *Venturia inaequalis* on apples, *Bipolaris* and *Drechslera* species on cereals, rice and lawns, *Septoria* species on wheat, *Botrytis cinerea* on strawberries, vegetables, ornamental plants and grapevines, *Mycosphaerella* species on bananas, peanuts and cereals, *Pseudocercosporella herpotrichoides* on wheat and barley, *Pyricularia oryzae* on rice, *Phaksopora pachyrizi*, and *P. meibomiae* on soya, *Phytophthora infestans* on potatoes and tomatoes, *Pseudoperonospora* species on cucurbits and hops, *Plasmopara viticola* on grapevines, *Alternaria* species on fruit and vegetables and also *Fusarium* and *Verticillium* species.

They can also be used in the protection of materials (e.g. the protection of wood), for example against *Paecilomyces variotii*.

The compounds I and II and the compounds III can be applied simultaneously, that is jointly or separately, or in succession, the sequence, in the case of separate application, generally not having any effect on the result of the control measures.

Suitable fungicidally active compounds III in the mixtures according to the invention are in particular fungicides selected from the following groups:

- acylalanines, such as benalaxyl, metalaxyl, ofurace, oxadixyl,
- amine derivatives, such as aldimorph, dodine, dodemorph, fenpropimorph, fenpropidin, guazatine, iminoctadine, spiroxamine, tridemorph,
- anilinopyrimidines, such as pyrimethanil, mepanipyrim or cyprodinil,
- antibiotics, such as cycloheximid, griseofulvin, kasugamycin, natamycin, polyoxin or streptomycin,
- azoles, such as bitertanol, bromoconazole, cyproconazole, difenoconazole, dinitroconazole, enilconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prochloraz, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizol, triticonazole,
- dicarboximides, such as iprodione, myclozolin, procymidone, vinclozolin,

- dithiocarbamates, such as ferbam, nabam, maneb, mancozeb, metam, metiram, propineb, polycarbamate, thiram, ziram, zineb,
- heterocyclic compounds, such as anilazine, benomyl, boscalid, carbendazim, carboxin, oxycarboxin, cyazofamid, dazomet, dithianon, famoxadone, fenamidone, fenarimol, fuberidazole, flutolanil, furametpyr, isoprothiolane, mepronil, nuarimol, picobenzamid, probenazole, proquinazid, pyrifenox, pyroquilon, quinoxyfen, silthiofam, thiabendazole, thifluzamide, thiophanate-methyl, tiadinil, tricyclazole, triforine,
- copper fungicides, such as Bordeaux mixture, copper acetate, copper oxychloride, basic copper sulfate,
- nitrophenyl derivatives, such as binapacryl, dinocap, dinobuton, nitrophthal-isopropyl,
- phenylpyrroles, such as fenpiclonil or fludioxonil,
- sulfur,
- other fungicides, such as acibenzolar-S-methyl, benthiavalicarb, carpropamid, chlorothalonil, cyflufenamid, cymoxanil, diclomezin, diclocymet, diethofencarb, edifenphos, ethaboxam, fenhexamid, fentin acetate, fenoxanil, ferimzone, fluazinam, phosphorous acid, fosetyl, fosetyl-aluminum, iprovalicarb, hexachlorobenzene, metrafenone, pencycuron, penthiopyrad, propamocarb, phthalide, tolclofos-methyl, quintozene, zoxamid,
- strobilurins, such as azoxystrobin, dimoxystrobin, enestroburin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, picoxystrobin, pyraclostrobin or trifloxystrobin,
- sulfenic acid derivatives, such as captafol, captan, dichlofluanid, folpet, tolylfluanid,
- cinnamides and analogous compounds, such as dimethomorph, flumetover or flumorph.

The active compounds III mentioned above, their preparation and their action against harmful fungi are generally known (cf.: http://www.hclrss.demon.co.uk/index.html); they are commercially available:

benalaxyl, methyl *N*-(phenylacetyl)-*N*-(2,6-xylyl)-DL-alaninate (DE 29 03 612),
metalaxyl, methyl *N*-(methoxyacetyl)-*N*-(2,6-xylyl)-DL-alaninate (GB 15 00 581);
ofurace, (*RS*)-*α*-(2-chloro-*N*-2,6-xylylacetamido)-*γ*-butyrolactone [CAS RN 58810-48-3];
oxadixyl; *N*-(2,6-dimethylphenyl)-2-methoxy-*N*-(2-oxo-3-oxazolidinyl)acetamide (GB 20 58 059);
aldimorph, "4-alkyl-2,5(or 2,6)-dimethylmorpholine", comprising 65-75% of 2,6-dimethylmorpholine and 25-35% of 2,5-dimethylmorpholine, comprising more than 85% of 4-dodecyl-2,5(or 2,6)-dimethylmorpholine, where "alkyl" also includes octyl, decyl, tetradecyl and hexadecyl, with a cis/trans ratio of 1:1 [CAS RN 91315-15-0];
dodine, 1-dodecylguanidinium acetate (Plant Dis. Rep., Vol. 41, p.1029 (1957));

dodemorph, 4-cyclododecyl-2,6-dimethylmorpholine (DE 1198125);
fenpropimorph, (*RS*)-*cis*-4-[3-(4-*tert*-butylphenyl)-2-methylpropyl]-2,6-dimethylmorpholine (DE 27 52 096);
fenpropidin, (*RS*)-1-[3-(4-*tert*-butylphenyl)-2-methylpropyl]piperidine (DE 27 52 096);
guazatine, mixture of the reaction products from the amidation of technical grade iminodi(octamethylene)diamine, comprising various guanidines and polyamines [CAS RN 108173-90-6];
iminoctadine, 1,1′-iminodi(octamethylene)diguanidine (Congr. Plant Pathol., 1., p.27 (1968);
spiroxamine, (8-tert-butyl-1,4-dioxaspiro[4.5]dec-2-yl)diethylamine (EP-A 281 842);
tridemorph, 2,6-dimethyl-4-tridecylmorpholine (DE 11 64 152);
pyrimethanil, 4,6-dimethylpyrimidin-2-ylphenylamine (DD-A 151 404);
mepanipyrim, (4-methyl-6-prop-1-ynylpyrimidin-2-yl)phenylamine (EP-A 224 339);
cyprodinil, (4-cyclopropyl-6-methylpyrimidin-2-yl)phenylamine (EP-A 310 550);
cycloheximid, 4-{(2*R*)-2-[(1*S*,3*S*,5*S*)-3,5-dimethyl-2-oxocyclohexyl]-2-hydroxyethyl}piperidine-2,6-dione [CAS RN 66-81-9];
griseofulvin, 7-chloro-2′,4,6-trimethoxy-6′-methylspiro[benzofuran-2(3*H*),1′-cyclohex-2′-ene]-3,4′-dione [CAS RN 126-07-8];
kasugamycin, 3-*O*-[2-amino-4-[(carboxyiminomethyl)amino]-2,3,4,6-tetradeoxy-α-D-*arabino*-hexopyranosyl]-D-*chiro*-inositol [CAS RN 6980-18-3];
natamycin, (8*E*,14*E*,16*E*,18*E*,20*E*)-(1*R*,3*S*,5*R*,7*R*,12*R*,22*R*,24*S*,25*R*,26*S*)-22-(3-amino-3,6-dideoxy-β-D-mannopyranosyloxy)-1,3,26-trihydroxy-12-methyl-10-oxo-6,11,28-trioxatricyclo[22.3.1.$0^{5,7}$]octacosa-8,14,16,18,20-pentaene-25-carboxylic acid [CAS RN 7681-93-8];
polyoxin, 5-(2-amino-5-*O*-carbamoyl-2-deoxy-L-xylonamido)-1-(5-carboxy-1,2,3,4-tetrahydro-2,4-dioxopyrimidin-1-yl)-1,5-dideoxy-β-D-allofuranuronic acid [CAS RN 22976-86-9];
streptomycin, 1,1′-{1-L-(1,3,5/2,4,6)-4-[5-deoxy-2-*O*-(2-deoxy-2-methylamino-α-L-glucopyranosyl)-3-*C*-formyl-α-L-lyxofuranosyloxy]-2,5,6-trihydroxycyclohex-1,3-ylene}diguanidine (J. Am. Chem. Soc. Vol. 69, p.1234 (1947));
bitertanol, β-([1,1′-biphenyl]-4-yloxy)-α-(1,1-dimethylethyl)-1*H*-1,2,4-triazole-1-ethanol (DE 23 24 020),
bromuconazole, 1-[[4-bromo-2-(2,4-dichlorophenyl)tetrahydro-2-furanyl]methyl]-1*H*-1,2,4-triazole (Proc. 1990 Br. Crop. Prot. Conf. – Pests Dis. Vol. 1, p. 459);
cyproconazole, 2-(4-chlorophenyl)-3-cyclopropyl-1-[1,2,4]triazol-1-ylbutan-2-ol (US 4 664 696);
difenoconazole, 1-{2-[2-chloro-4-(4-chlorophenoxy)phenyl]-4-methyl-[1,3]dioxolan-2-ylmethyl}-1H-[1,2,4]triazole (GB-A 2 098 607);
diniconazole, (βE)-β-[(2,4-dichlorophenyl)methylene]-α-(1,1-dimethylethyl)-1*H*-1,2,4-triazole-1-ethanol (Noyaku Kagaku, 1983, Vol. 8, p. 575);

enilconazole (imazalil), 1-[2-(2,4-dichlorphenyl)-2-(2-propenyloxy)ethyl]-1*H*-imidazole (Fruits, 1973, Vol. 28, p. 545);
epoxiconazole, (2*RS*,3*SR*)-1-[3-(2-chlorophenyl)-2,3-epoxy-2-(4-fluorophenyl)propyl]-1*H*-1,2,4-triazole (EP-A 196 038);
fenbuconazole, α-[2-(4-chlorophenyl)ethyl]-α-phenyl-1*H*-1,2,4-triazole-1-propanenitrile (Proc. 1988 Br. Crop Prot. Conf. – Pests Dis. Vol. 1, p. 33);
fluquinconazole, 3-(2,4-dichlorophenyl)-6-fluoro-2-[1,2,4]–triazol-1-yl-3H-quinazolin-4-one (Proc. Br. Crop Prot. Conf.-Pests Dis., 5-3, 411 (1992));
flusilazole, 1-{[bis-(4-fluorophenyl)methylsilanyl]methyl}-1H-[1,2,4]triazole (Proc. Br. Crop Prot. Conf.-Pests Dis., 1, 413 (1984));
flutriafol, α-(2-fluorophenyl)-α-(4-fluorophenyl)-1*H*-1,2,4-triazole-1-ethanol (EP 15 756);
hexaconazole, 2-(2,4-dichlorophenyl)-1-[1,2,4]triazol-1-ylhexan-2-ol (CAS RN 79983-71-4);
ipconazole, 2-[(4-chlorophenyl)methyl]-5-(1-methylethyl)-1-(1*H*-1,2,4-triazol-1-yl-methyl)cyclopentanol (EP 267 778),
metconazole, 5-(4-chlorobenzyl)-2,2-dimethyl-1-[1,2,4]triazol-1-ylmethylcyclopentanol (GB 857 383);
myclobutanil, 2-(4-chlorophenyl)-2-[1,2,4]triazol-1-ylmethylpentanenitrile (CAS RN 88671–89–0);
penconazole, 1-[2-(2,4-dichlorophenyl)pentyl]-1H-[1,2,4]triazole (Pesticide Manual, 12th Ed. (2000), S.712);
propiconazole, 1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1*H*-1,2,4-triazole (BE 835 579);
prochloraz, N-(propyl-[2-(2,4,6-trichlorophenoxy)ethyl])imidazole-1-carboxamide (US 3 991 071);
prothioconazole, 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]triazole-3-thione (WO 96/16048);
simeconazole, α-(4-fluorophenyl)-α-[(trimethylsilyl)methyl]-1*H*-1,2,4-triazole-1-ethanol [CAS RN 149508-90-7],
tebuconazole, 1-(4-chlorophenyl)-4,4-dimethyl-3-[1,2,4]triazol-1-ylmethylpentan-3-ol (EP-A 40 345);
tetraconazole, 1-[2-(2,4-dichlorophenyl)-3-(1,1,2,2-tetrafluoroethoxy)propyl]-1*H*-1,2,4-triazole (EP 234 242);
triadimefon, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone (BE 793 867);
triadimenol, β-(4-chlorophenoxy)-α-(1,1-dimethylethyl)-1*H*-1,2,4-triazole-1-ethanol (DE 23 24 010);
triflumizol, (4-chloro-2-trifluormethylphenyl)-(2-propoxy-1-[1,2,4]triazol-1-ylethyliden)-amine (JP-A 79/119 462);

triticonazole, (5*E*)-5-[(4-chlorophenyl)methylene]-2,2-dimethyl-1-(1*H*-1,2,4-triazol-1-ylmethyl)cyclopentanol (FR 26 41 277);
iprodione, N-isopropyl-3-(3,5-dichlorophenyl)-2,4-dioxoimidazolidine-1-carboxamide (GB 13 12 536);
myclozolin, (*RS*)-3-(3,5-dichlorophenyl)-5-methoxymethyl-5-methyl-1,3-oxazolidine-2,4-dione [CAS RN 54864-61-8];
procymidone, *N*-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide (US 3 903 090);
vinclozolin, 3-(3,5-dichlorophenyl)-5-methyl-5-vinyloxazolidine-2,4-dione (DE-A 22 07 576);
ferbam, iron(3+) dimethyldithiocarbamate (US 1 972 961);
nabam, disodium ethylenebis(dithiocarbamate) (US 2 317 765);
maneb, manganese ethylenebis(dithiocarbamate) (US 2 504 404);
mancozeb, manganese ethylenebis(dithiocarbamate) polymer complex zinc salt (GB 996 264);
metam, methyldithiocarbaminic acid (US 2 791 605);
metiram, zinc ammoniate ethylenebis(dithiocarbamate) (US 3 248 400);
propineb, zinc propylenebis(dithiocarbamate) polymer (BE 611 960);
polycarbamate, bis(dimethylcarbamodithioato-$\kappa S,\kappa S'$)[μ-[[1,2-ethanediylbis[carbamodithioato-$\kappa S,\kappa S'$]](2−)]]di[zinc] [CAS RN 64440-88-6];
thiram, bis(dimethylthiocarbamoyl) disulfide (DE 642 532);
ziram, dimethyldithiocarbamate [CAS RN 137-30-4];
zineb, zinc ethylenebis(dithiocarbamate) (US 2 457 674);
anilazine, 4,6-dichloro-*N*-(2-chlorophenyl)-1,3,5-triazine-2-amine (US 2 720 480);
benomyl, N-butyl-2-acetylaminobenzoimidazole-1-carboxamide (US 3 631 176);
boscalid, 2-chloro-*N*-(4'-chlorobiphenyl-2-yl)nicotinamide (EP-A 545 099);
carbendazim, methyl (1H-benzoimidazol-2-yl)carbamate (US 3 657 443);
carboxin, 5,6-dihydro-2-methyl-*N*-phenyl-1,4-oxathiin-3-carboxamide (US 3 249 499);
oxycarboxin, 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide 4,4-dioxide (US 3 399 214);
cyazofamid, 4-chloro-2-cyano-*N,N*-dimethyl-5-(4-methylphenyl)-1*H*-imidazole-1-sulfonamide (CAS RN 120116-88-3];
dazomet, 3,5-dimethyl-1,3,5-thiadiazinane-2-thione (Bull. Soc. Chim. Fr. Vol. 15, p. 891 (1897));
dithianon, 5,10-dioxo-5,10-dihydronaphtho[2,3-b][1,4]dithiin-2,3-dicarbonitrile (GB 857 383);
famoxadone, (*RS*)-3-anilino-5-methyl-5-(4-phenoxyphenyl)-1,3-oxazolidine-2,4-dione [CAS RN 131807-57-3];
fenamidone, (*S*)-1-anilino-4-methyl-2-methylthio-4-phenylimidazolin-5-one [CAS RN 161326-34-7];

fenarimol, α-(2-chlorophenyl)-α-(4-chlorophenyl)-5-pyrimidinemethanol (GB 12 18 623);
fuberidazole, 2-(2-furanyl)-1*H*-benzimidazole (DE 12 09 799);
flutolanil, α,α,α-trifluoro-3'-isopropoxy-*o*-toluanilide (JP 1104514);
furametpyr, 5-chloro-*N*-(1,3-dihydro-1,1,3-trimethyl-4-isobenzofuranyl)-1,3-dimethyl-1*H*-pyrazole-4-carboxamide [CAS RN 123572-88-3];
isoprothiolane, diisopropyl 1,3-dithiolan-2-ylidenemalonate (Proc. Insectic. Fungic. Conf. 8. Vol. 2, p. 715 (1975));
mepronil, 3'-isopropoxy-*o*-toluanilide (US 3 937 840);
nuarimol, α-(2-chlorophenyl)-α-(4-fluorophenyl)-5-pyrimidinemethanol (GB 12 18 623);
fluopicolide (picobenzamid), 2,6-dichloro-N-(3-chloro-5-trifluoromethylpyridin-2-ylmethyl)benzamide (WO 99/42447);
probenazole, 3-allyloxy-1,2-benzothiazole 1,1-dioxide (Agric. Biol. Chem. Vol. 37, p. 737 (1973));
proquinazid, 6-iodo-2-propoxy-3-propylquinazolin-4(3*H*)-one (WO 97/48684);
pyrifenox, 2',4'-dichloro-2-(3-pyridyl)acetophenone (*EZ*)-*O*-methyloxime (EP 49 854);
pyroquilon, 1,2,5,6-tetrahydropyrrolo[3,2,1-*ij*]quinolin-4-one (GB 139 43 373)
quinoxyfen, 5,7-dichloro-4-(4-fluorophenoxy)quinoline (US 5 240 940);
silthiofam, *N*-allyl-4,5-dimethyl-2-(trimethylsilyl)thiophene-3-carboxamide [CAS RN 175217-20-6];
thiabendazole, 2-(1,3-thiazol-4-yl)benzimidazole (US 3 017 415);
thifluzamide, 2',6'-dibromo-2-methyl-4'-trifluormethoxy-4-trifluormethyl-1,3-thiazole-5-carboxanilide [CAS RN 130000-40-7];
thiophanate-methyl, 1,2-phenylenebis(iminocarbonothioyl)bis(dimethylcarbamate) (DE-A 19 30 540);
tiadinil, 3'-chloro-4,4'-dimethyl-1,2,3-thiadiazole-5-carboxanilide [CAS RN 223580-51-6];
tricyclazole, 5-methyl-1,2,4-triazolo[3,4-*b*][1,3]benzothiazole [CAS RN 41814-78-2];
triforine, *N,N'*-{piperazine-1,4-diylbis[(trichlormethyl)methylene]}diformamide (DE 19 01 421);
Bordeaux mixture, mixture of $CuSO_4$ x $3Cu(OH)_2$ x $3CaSO_4$ [CAS RN 8011-63-0]
copper acetate, $Cu(OCOCH_3)_2$ [CAS RN 8011-63-0];
copper oxychloride, $Cu_2Cl(OH)_3$ [CAS RN 1332-40-7];
basic copper sulfate, $CuSO_4$ [CAS RN 1344-73-6];
binapacryl, (*RS*)-2-*sec*-butyl-4,6-dinitrophenyl 3-methylcrotonate [CAS RN 485-31-4];
dinocap, the mixture of 2,6-dinitro-4-octylphenylcrotonate and 2,4-dinitro-6-octyl-phenylcrotonate, where "octyl" is a mixture of 1-methylheptyl, 1-ethylhexyl and 1-propylpentyl (US 2 526 660);
dinobuton, (*RS*)-2-*sec*-butyl-4,6-dinitrophenyl isopropyl carbonate [CAS RN 973-21-7];
nitrothal-isopropyl, diisopropyl 5-nitroisophthalate (Proc. Br. Insectic. Fungic. Conf. 7., Vol. 2, p. 673 (1973));

fenpiclonil, 4-(2,3-dichlorophenyl)-1H-pyrrole-3-carbonitrile (Proc. 1988 Br. Crop Prot. Conf. – Pests Dis., Vol. 1, p. 65);
fludioxonil, 4-(2,2-difluorobenzo[1,3]dioxol-4-yl)-1H-pyrrole-3-carbonitrile (The Pesticide Manual, publ. The British Crop Protection Council, 10th ed. (1995), p. 482);
acibenzolar-S-methyl, methyl 1,2,3-benzothiadiazol-7-carbothioate [CAS RN 135158-54-2];
flubenthiavalicarb (benthiavalicarb), isopropyl {(S)-1-[(1R)-1-(6-fluorobenzothiazol-2-yl)-ethylcarbamoyl]-2-methylpropyl}carbamate (JP-A 09/323 984);
carpropamid, 2,2-dichloro-*N*-[1-(4-chlorphenyl)ethyl]-1-ethyl-3-methylcyclopropane-carboxamide [CAS RN 104030-54-8];
chlorothalonil, 2,4,5,6-tetrachloroisophthalonitrile (US 3 290 353);
cyflufenamid, (*Z*)-*N*-[*α*-(cyclopropylmethoxyimino)-2,3-difluoro-6-(trifluoromethyl)benzyl]-2-phenylacetamide (WO 96/19442);
cymoxanil, 1-(2-cyano-2-methoxyiminoacetyl)-3-ethylurea (US 3 957 847);
diclomezine, 6-(3,5-dichlorophenyl-*p*-tolyl)pyridazin-3(2*H*)-one (US 4 052 395)
diclocymet, (*RS*)-2-cyano-*N*-[(*R*)-1-(2,4-dichlorophenyl)ethyl]-3,3-dimethylbutyramide [CAS RN 139920-32-4];
diethofencarb, isopropyl 3,4-diethoxycarbanilate (EP 78 663);
edifenphos, *O*-ethyl *S,S*-diphenyl phosphorodithioate (DE 14 93 736)
ethaboxam, *N*-(cyano-2-thienylmethyl)-4-ethyl-2-(ethylamino)-5-thiazolecarboxamide (EP-A 639 574);
fenhexamid, N-(2,3-dichloro-4-hydroxyphenyl)-1-methylcyclohexanecarboxamide (Proc. Br. Crop Prot. Conf. – Pests Dis., 1998, Vol. 2, p. 327);
fentin acetate, triphenyltin (US 3 499 086);
fenoxanil, *N*-(1-cyano-1,2-dimethylpropyl)-2-(2,4-dichlorophenoxy)propanamide (EP 262 393);
ferimzone, (*Z*)-2′-methylacetophenone-4,6-dimethylpyrimidin-2-ylhydrazone [CAS RN 89269-64-7];
fluazinam, 3-chloro-N-[3-chloro-2,6-dinitro-4-(trifluoromethyl)phenyl]-5-(trifluoromethyl)-2-pyridinamine (The Pesticide Manual, publ. The British Crop Protection Council, 10th ed. (1995), p. 474);
fosetyl, fosetyl-aluminum, ethylphosphonate (FR 22 54 276);
iprovalicarb, isopropyl [(1S)-2-methyl-1-(1-p-tolylethylcarbamoyl)propyl]carbamate (EP-A 472 996);
hexachlorbenzene (C. R. Seances Acad. Agric. Fr., Vol. 31, p. 24 (1945);
metrafenon, 3′-bromo-2,3,4,6′-tetramethoxy-2′,6-dimethylbenzophenone (US 5 945 567);
pencycuron, 1-(4-chlorobenzyl)-1-cyclopentyl-3-phenylurea (DE 27 32 257);
penthiopyrad, (*RS*)-*N*-[2-(1,3-dimethylbutyl)-3-thienyl]-1-methyl-3-(trifluoromethyl)-1*H*-pyrazole-4-carboxamide (JP 10130268);

propamocarb, propyl 3-(dimethylamino)propylcarbamate (DE 15 67 169);
phthalide (DE 16 43 347);
toloclofos-methyl, *O*-2,6-dichloro-*p*-tolyl *O,O*-dimethyl phosphorothioate (GB 14 67 561);
quintozene, pentachlornitrobenzene (DE 682 048);
zoxamide, (*RS*)-3,5-dichloro-*N*-(3-chloro-1-ethyl-1-methyl-2-oxopropyl)-*p*-toluamide [CAS RN 156052-68-5];
azoxystrobin, methyl 2-{2-[6-(2-cyano-1-vinylpenta-1,3-dienyloxy)pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate (EP 382 375),
dimoxystrobin, (*E*)-2-(methoxyimino)-*N*-methyl-2-[*α*-(2,5-xylyloxy)-*o*-tolyl]acetamide (EP 477 631);
enestroburin, methyl 2-{2-[3-(4-chlorophenyl)-1-methylallylideneaminooxymethyl]-phenyl}-3-methoxyacrylate (EP 936 213);
fluoxastrobin, (*E*)-{2-[6-(2-chlorophenoxy)-5-fluoropyrimidin-4-yloxy]phenyl}(5,6-dihydro-1,4,2-dioxazin-3-yl)methanone *O*-methyloxime (WO 97/27189);
kresoxim-methyl, methyl (*E*)-methoxyimino[*α*-(*o*-tolyloxy)-*o*-tolyl]acetate (EP 253 213);
metominostrobin, (*E*)-2-(methoxyimino)-*N*-methyl-2-(2-phenoxyphenyl)acetamide (EP 398 692);
orysastrobin, (2*E*)-2-(methoxyimino)-2-{2-[(3*E*,5*E*,6*E*)-5-(methoxyimino)-4,6-dimethyl-2,8-dioxa-3,7-diazanona-3,6-dien-1-yl]phenyl}-*N*-methylacetamide (WO 97/15552);
picoxystrobin, methyl 3-methoxy-2-[2-(6-trifluoromethylpyridin-2-yloxymethyl)phenyl]-acrylate (EP 278 595);
pyraclostrobin, methyl *N*-{2-[1-(4-chlorophenyl)-1*H*-pyrazol-3-yloxymethyl]phenyl}(*N*-methoxy)carbamate (WO 96/01256);
trifloxystrobin, methyl (*E*)-methoxyimino-{(*E*)-*α*-[1-(*α*,*α*,*α*-trifluoro-*m*-tolyl)ethylidene-aminooxy]-*o*-tolyl}acetate (EP 460 575);
captafol, *N*-(1,1,2,2-tetrachloroethylthio)cyclohex-4-ene-1,2-dicarboximide (Phytopathology, Vol. 52, p. 754 (1962));
captan, *N*-(trichloromethylthio)cyclohex-4-ene-1,2-dicarboximide (US 2 553 770);
dichlofluanid, N-dichlorofluoromethylthio-*N'*,*N'*-dimethyl-*N*-phenylsulfamide (DE 11 93 498);
folpet, *N*-(trichlormethylthio)phthalimide (US 2 553 770);
tolylfluanid, *N*-dichlorofluoromethylthio-*N'*,*N'*-dimethyl-*N*-*p*-tolylsulfamide (DE 11 93 498);
dimethomorph, 3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)-1-morpholin-4-yl-propenone (EP 120 321);
flumetover, 2-(3,4-dimethoxyphenyl)-*N*-ethyl-*α*,*α*,*α*-trifluoro-*N*-methyl-*p*-toluamide [A-GROW no. 243, 22 (1995)];
flumorph, 3-(4-fluorophenyl)-3-(3,4-dimethoxyphenyl)-1-morpholin-4-ylpropenone (EP 860 438).

Preference is given to mixtures of the compounds I and II with an active compound III selected from the above-mentioned anilinopyrimidines, azoles, dithiocarbamates, heterocyclic compounds, sulfenic acid derivatives, cinnamic acid derivatives or the other fungicides mentioned, in particular the azoles mentioned.

Particular preference is given to mixtures of the compounds I and II with an active compound III selected from the group consisting of cyprodinil, epoxiconazole, fluquinconazole, metconazole, prochloraz, prothioconazole, tebuconazole, triticonazole, mancozeb, metiram, boscalid, dithianon, chlorothalonil, metrafenone, propamocarb, folpet and dimethomorph.

In one embodiment of the mixtures according to the invention, a further fungicide IV is added to the compounds II and III. Suitable components IV are the active compounds III mentioned above.

Mixtures of the compounds I and II with one component III are preferred.

The compounds I, II and III are usually applied in a weight ratio of from 100:1:5 to 1:100:20, preferably from 20:1:1 to 1:20:20 to 1:20:1 to 20:1:20, in particular from 10:1:1 to 1:10:10 to 1:10:1 to 10:1:10.

The components IV are, if desired, added in a ratio of from 20:1 to 1:20 to the mixtures of the compounds I, II and III.

Depending on the type of compound and the desired effect, the application rates of the mixtures according to the invention are from 5 g/ha to 2500 g/ha, preferably from 5 g/ha to 1000 g/ha, in particular from 50 to 750 g/ha.

Correspondingly, the application rates for the compound I are generally from 1 to 1000 g/ha, preferably from 10 to 900 g/ha, in particular from 20 to 750 g/ha.

Correspondingly, the application rates for the compounds II are generally from 1 to 1000 g/ha, preferably from 10 to 500 g/ha, in particular from 40 to 350 g/ha.

Correspondingly, the application rates for the compounds III are generally from 1 to 1000 g/ha, preferably from 10 to 500 g/ha, in particular from 40 to 350 g/ha.

In the treatment of seed, application rates of mixture are generally from 1 to 1000 g/100 kg of seed, preferably from 1 to 200 g/100 kg, in particular from 5 to 100 g/100 kg.

The method for controlling harmful fungi is carried out by the separate or joint application of the compounds I and II and a compound III or of the mixtures of the compounds I, II and a compound III, by spraying or dusting the seeds, the plants or the soil before or after sowing of the plants or before or after emergence of the plants.

The mixtures according to the invention, or the compounds I, II and III, can be converted into the customary formulations, for example solutions, emulsions, suspensions, dusts, powders, pastes and granules. The use form depends on the particular intended purpose; in each case, it should ensure a fine and even distribution of the compound according to the invention.

The formulations are prepared in a known manner, for example by extending the active compound with solvents and/or carriers, if desired using emulsifiers and dispersants. Solvents/auxiliaries suitable for this purpose are essentially:

- water, aromatic solvents (for example Solvesso products, xylene), paraffins (for example mineral oil fractions), alcohols (for example methanol, butanol, pentanol, benzyl alcohol), ketones (for example cyclohexanone, gamma-butyrolactone), pyrrolidones (NMP, NOP), acetates (glycol diacetate), glycols, fatty acid dimethylamides, fatty acids and fatty acid esters. In principle, solvent mixtures may also be used.
- carriers such as ground natural minerals (for example kaolins, clays, talc, chalk) and ground synthetic minerals (for example highly disperse silica, silicates); emulsifiers such as nonionogenic and anionic emulsifiers (for example polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignosulfite waste liquors and methylcellulose.

Suitable surfactants used are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutylnaphthalene-]sulfonic acid, alkylarylsulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates, fatty acids and sulfated fatty alcohol glycol ethers, furthermore condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctylphenol, octylphenol, nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ether, tristearylphenyl polyglycol ether, alkylaryl polyether alcohols, alcohol and fatty alcohol ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers,

ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lignosulfite waste liquors and methylcellulose.

Substances which are suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, cyclohexanol, cyclohexanone, isophorone, highly polar solvents, for example dimethyl sulfoxide, N-methylpyrrolidone and water.

Powders, materials for spreading and dustable products can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.

Granules, for example coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active compounds to solid carriers. Examples of solid carriers are mineral earths such as silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, such as, for example, ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

In general, the formulations comprise from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active compounds. The active compounds are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

The following are examples of formulations: 1. Products for dilution with water

A) Water-soluble concentrates (SL)
10 parts by weight of the active compounds are dissolved in water or in a water-soluble solvent. As an alternative, wetters or other auxiliaries are added. The active compound dissolves upon dilution with water.

B) Dispersible concentrates (DC)
20 parts by weight of the active compounds are dissolved in cyclohexanone with addition of a dispersant, for example polyvinylpyrrolidone. Dilution with water gives a dispersion.

C) Emulsifiable concentrates (EC)

15 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength). Dilution with water gives an emulsion.

D) Emulsions (EW, EO)

40 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength). This mixture is introduced into water by means of an emulsifying machine (Ultraturrax) and made into a homogeneous emulsion. Dilution with water gives an emulsion.

E) Suspensions (SC, OD)

In an agitated ball mill, 20 parts by weight of the active compounds are comminuted with addition of dispersants, wetters and water or an organic solvent to give a fine active compound suspension. Dilution with water gives a stable suspension of the active compound.

F) Water-dispersible granules and water-soluble granules (WG, SG)

50 parts by weight of the active compounds are ground finely with addition of dispersants and wetters and prepared as water-dispersible or water-soluble granules by means of technical appliances (for example extrusion, spray tower, fluidized bed). Dilution with water gives a stable dispersion or solution of the active compound.

G) Water-dispersible powders and water-soluble powders (WP, SP)

75 parts by weight of the active compounds are ground in a rotor-stator mill with addition of dispersants, wetters and silica gel. Dilution with water gives a stable dispersion or solution of the active compound.

2. Products to be applied undiluted

H) Dustable powders (DP)

5 parts by weight of the active compounds are ground finely and mixed intimately with 95% of finely divided kaolin. This gives a dustable product.

I) Granules (GR, FG, GG, MG)

0.5 part by weight of the active compounds is ground finely and associated with 95.5% carriers. Current methods are extrusion, spray-drying or the fluidized bed. This gives granules to be applied undiluted.

J) ULV solutions (UL)

10 parts by weight of the active compounds are dissolved in an organic solvent, for example xylene. This gives a product to be applied undiluted.

The active compounds can be used as such, in the form of their formulations or the use forms prepared therefrom, for example in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dustable products, materials for spreading, or granules, by means of spraying, atomizing, dusting, spreading or pouring. The use forms depend entirely on the intended purposes; they are intended to ensure in each case the finest possible distribution of the active compounds according to the invention.

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of a wetter, tackifier, dispersant or emulsifier. However, it is also possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

The active compound concentrations in the ready-to-use preparations can be varied within relatively wide ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

The active compounds may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active compound, or even to apply the active compound without additives.

Oils of various types, wetters, adjuvants, herbicides, fungicides, other pesticides, or bactericides may be added to the active compounds, even, if appropriate, not until immediately prior to use (tank mix). These agents are typically admixed with the compositions according to the invention in a weight ratio of from 1:10 to 10:1.

The compounds I and II or the mixtures or the corresponding formulations are applied by treating the harmful fungi, the plants, seeds, soils, areas, materials or spaces to be kept free from them with a fungicidally effective amount of the mixture or, in the case of separate application, of the compounds I and II. Application can be carried out before or after infection by the harmful fungi.

The fungicidal effect of the compound and the mixtures is demonstrated by the following tests:

The active compounds were prepared as a stock solution with 25 mg of active compound which was made up to 10 ml using a mixture of acetone and/or DMSO and the emulsifier Uniperol® EL (wetting agent having emulsifying and dispersing action based on ethoxylated alkylphenols) in a volume ratio of solvent/emulsifier of 99 to 1. The mixture was then made up with water to 100 ml. This stock solution was diluted with the solvent/emulsifier/water mixture described to the concentration of active compounds stated below.

Use example 1 - Activity against net blotch of barley caused by *Pyrenophora teres,* 1 day protective application

Leaves of potted barley seedlings of the cultivar "Hanna" were sprayed to runoff point with an aqueous suspension having the concentration of active compound stated below. 24 hours after the spray coating had dried on, the test plants were inoculated with an aqueous spore suspension of *Pyrenophora [syn. Drechslera] teres,* the net blotch pathogen. The test plants were then placed in a greenhouse at temperatures between 20 and 24°C and 95 to 100% relative atmospheric humidity. After 6 days, the extent of the development of the disease was determined visually in % infection of the entire leaf area.

The visually determined percentages of infected leaf areas were converted into efficacies in % of the untreated control:

The efficacy (E) is calculated as follows using Abbot's formula:

$$E = (1 - \alpha/\beta) \cdot 100$$

α corresponds to the fungicidal infection of the treated plants in % and

β corresponds to the fungicidal infection of the untreated (control) plants in %

An efficacy of 0 means that the infection level of the treated plants corresponds to that of the untreated control plants; an efficacy of 100 means that the treated plants were not infected.

The expected efficacies of mixtures of active compounds were determined using Colby's formula (Colby, S.R. "Calculating synergistic and antagonistic responses of herbicide combinations", Weeds, 15, 20-22, 1967) and compared with the observed efficacies.

Colby's formula:

$$E = x + y - x \cdot y/100$$

E expected efficacy, expressed in % of the untreated control, when using the mixture of the active compounds (I+II) and III at the concentrations a and b

x efficacy, expressed in % of the untreated control, when using the active compound combination (I+II) at the concentration a

y efficacy, expressed in % of the untreated control, when using the active compound III at the concentration b

Table A – Binary combination / individual active compounds

Example	Active compound / mixing ratio	Concentration of active compound in the spray liquor [ppm]	Efficacy in % of the untrated control
1	control (untreated)	-	(90 % infected)
2	I + II.1 (1:1)	12.5 + 12.5 6.25 + 6.25 3.1 + 3.1 1.6 + 1.6	83 67 56 44
3	prochloraz	25 12.5	0 0

Table B – Mixtures according to the invention

Example	Active compound mixture concentration mixing ratio	Observed efficacy	Calculated efficacy *)
4	I + II.1 + prochloraz 12.5 + 12.5 + 25 ppm 1:1:2	94	83
5	I + II.1 + prochloraz 6.25 + 6.25 + 12.5 ppm 1:1:2	83	67
6	I + II.1 + prochloraz 6.25 + 6.25 + 25 ppm 1:1:4	89	67
7	I + II.1 + prochloraz 3.1 + 3.1 + 12.5 ppm 1:1:4	83	56

Example	Active compound mixture concentration mixing ratio	Observed efficacy	Calculated efficacy *)
8	I + II.1 + prochloraz 3.1 + 3.1 + 25 ppm 1:1:8	89	56
9	I + II.1 + prochloraz 1.6 + 1.6 + 12.5 ppm 1:1:8	78	44

*) efficacy calculated using Colby's formula

Use example 2 - Activity against Septoria nodorum blotch of wheat caused by *Leptosphaeria nodorum*

Pots with wheat plants of the cultivar "Kanzler" were sprayed to runoff point with an aqueous suspension having the concentration of active compound stated below. The next day, the pots were inoculated with an aqueous spore suspension of *Leptosphaeria nodorum (syn. Stagonospora nodorum, Septoria nodorum)*. The plants were then placed in a chamber at 20°C and maximum atmospheric humidity. After 8 days, the Septoria nodorum blotch on the untreated but infected control plants had developed to such an extent that the degree of infection could be determined visually in %.

Evaluation was carried out analogously to Example 1.

Table C – Binary combination / individual active compounds

Example	Active compound / mixing ratio	Concentration of active compound in the spray liquor [ppm]	Efficacy in % of the untrated control
10	control (untreated)	-	(90 % infected)
11	I + II.1 (1:1)	1.6 + 1.6	44
12	boscalid	12.5 3.1 1.6	33 11 0
13	metconazole	1.6 0.8 0.4	56 0 0
14	epoxiconazole	1.6 0.8 0.4	33 0 0

Table D – Mixtures according to the invention

Example	Active compound mixture concentration mixing ratio	Observed efficacy	Calculated efficacy *)
15	I + II.1 + boscalid 1.6 + 1.6 + 1.6 ppm 1:1:1	67	44
16	I + II.1 + boscalid 1.6 + 1.6 + 3.1 ppm 1:1:2	78	51
17	I + II.1 + boscalid 1.6 + 1.6 + 12.5 ppm 1:1:8	89	63
18	I + II.1 + metconazole 1.6 + 1.6 + 1.6 ppm 1:1:1	89	75
19	I + II.1 + metconazole 1.6 + 1.6 + 0.8 ppm 2:2:1	83	44
20	I + II.1 + metconazole 0.8 + 0.8 + 0.4 ppm 2:2:1	56	11
21	I + II.1 + epoxiconazole 1.6 + 1.6 + 1.6 ppm 1:1:1	94	63
22	I + II.1 + epoxiconazole 1.6 + 1.6 + 0.8 ppm 2:2:1	89	44
23	I + II.1 + epoxiconazole 0.8 + 0.8 + 0.4 ppm 2:2:1	33	11

*) efficacy calculated using Colby's formula

Use example 3 – Persistency against early blight on tomatoes caused by *Alternaria solani*, 5 day protective treatment

Leaves of potted plants were sprayed to runoff point with an aqueous suspension having the concentration of active compound stated below. To test for persistency, the leaves were infected with an aqueous spore suspension of *Alternaria solani* in a 2% strength

biomalt solution having a density of 0.17 x 10^6 spores/ml only after 5 days. The plants were then placed in a water-vapor-saturated chamber at temperatures between 20 and 22°C. After a further 5 days the disease on the treated but infected control plants had developed to such an extent that the infection could be determined visually in %.

Evaluation was carried out analogously to Example 1.

Table E – Binary combination / individual active compounds

Example	Active compound / mixing ratio	Concentration of active compound in the spray liquor [ppm]	Efficacy in % of the untrated control
24	control (untreated)	-	(80 % infected)
25	I + II.1 (1:1)	12.5 + 12.5 6.25 + 6.25 3.1 + 3.1	25 13 0
26	I + II.2 (1:1)	25 + 25	13
27	boscalid	6.25	0
28	prochloraz	25 12.5	0 0
29	epoxiconazole	25 6.25 3.1 1.6 0.8	0 0 0 0 0

Table F – Mixtures according to the invention

Example	Active compound mixture concentration mixing ratio	Observed efficacy	Calculated efficacy *)
30	I + II.1 + boscalid 6.25 + 6.25 + 6.25 ppm 1:1:1	96	13
31	I + II.1 + boscalid 3.1 + 3.1 + 6.25 ppm 1:1:2	63	0
32	I + II.1 + epoxiconazole 6.25 + 6.25 + 6.25 ppm 1:1:1	63	13

Example	Active compound mixture concentration mixing ratio	Observed efficacy	Calculated efficacy *)
33	I + II.1 + epoxiconazole 12.5 + 12.5 + 3.1 ppm 4:4:1	96	25
34	I + II.1 + epoxiconazole 6.25 + 6.25 + 1.6 ppm 4:4:1	38	13
35	I + II.1 + epoxiconazole 12.5 + 12.5 + 1.6 ppm 8:8:1	81	25
36	I + II.1 + epoxiconazole 12.5 + 12.5 + 0.8 ppm 16:16:1	69	25
37	I + II.1 + prochloraz 12.5 + 12.5 + 12.5 ppm 1:1:1	75	25
48	I + II.1 + prochloraz 6.25 + 6.25 + 12.5 ppm 1:1:2	50	13
39	I + II.1 + prochloraz 6.25 + 6.25 + 25 ppm 1:1:4	81	13
40	I + II.1 + prochloraz 3.1 + 3.1 + 25 ppm 1:1:8	50	0
41	I + II.2 + epoxiconazole 25 + 25 + 25 ppm 1:1:1	50	13
42	I + II.2 + epoxiconazole 25 + 25 + 6.25 ppm 4:4:1	38	13

*) efficacy calculated using Colby's formula

The test results show that, by virtue of the strong synergism, the mixtures according to the invention in all mixing ratios are considerably more active than had been predicted using Colby's formula.